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(54) Title: MODIFIED PIGMENTS HAVING IMPROVED DISPERSING PROPERTIES		
(57) Abstract <p>Various modified pigment products are described which are preferably capable of being dispersed in a variety of materials such as coatings, inks, toners, films, plastics, polymers, elastomers, and the like. The modified pigments are pigments having attached groups, such as polymeric groups, onto the pigment by means other than adsorption. A modified pigment product is described comprising a pigment having attached at least one group comprising the formula: $-X-[Nion]_pR$, wherein X comprises an aromatic group or an alkyl group, Nion comprises at least one type of non-ionic group, R represents hydrogen or comprises an aromatic group or an alkyl group, and p represents an integer of from 1 to 500. Modified pigment products are also described comprising a pigment having attached at least one alkylene oxide group or at least one polymeric group. In addition, other types of modified pigment products are described as well as their incorporation into inks, coatings, toners, films, plastics, polymers, elastomers, and the like. Methods of making the modified pigment products are also described.</p>		

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MODIFIED PIGMENTS HAVING IMPROVED DISPERSING PROPERTIES

BACKGROUND OF THE INVENTION

The present invention relates to pigments which can be used in a variety of applications, and more particularly relates to the modification of pigments to improve various properties.

5 Pigments have been used in a variety of applications, such as in inks, coatings, toners, plastics, rubber, films, and the like. Common goals in each of these applications are to provide a pigment which is capable of being substantially and uniformly dispersed, and capable of remaining dispersed in the composition so that color and other properties exhibited by the pigment are uniform throughout the composition or material which incorporates the pigment. The improvement in the dispersibility and dispersion stability of pigments has been attempted previously and has included coating or adsorbing various surfactants onto the pigment. However, merely adsorbing or coating pigments had potentially several disadvantages. First, adsorbed surfactants are dependent on the physical properties of the surrounding materials, such as the solvent with the ink. In such a situation, an equilibrium may exist between the surface of the pigment and the solvent for surfactant affinity. Solubility issues involving the surfactant and the solvent may also come into effect. Other considerations which can effect adsorbed surfactants are the concentration of the pigment, the type of surfactants used, and the temperature and pH of the composition or material containing the pigment. Any one or more of these physical properties can cause the removal of the surfactant from the surface of the pigment and create additional surfactant in the bulk liquid or medium which may negatively effect the dispersion stability and other properties of the bulk liquid such as foaming, surface tension, viscosity, film strength, film elasticity, and the like. In addition, the excess surfactant which may be found in conventional pigments may also be detrimental to plastic or film-forming properties, such as color, strength, elongation, elasticity, and the like. Accordingly, there is a desire in the art to improve the dispersibility and dispersion stability of pigments with respect to overcoming one or more of the above-described disadvantages.

SUMMARY OF THE INVENTION

25 A feature of the present invention is to provide modified pigment products which are capable of improving the dispersibility and dispersion stability of the pigment in compositions and formulations.

30 Another feature of the present invention is to provide ink, coating, toner, polymer, paper, film, and rubber formulations which incorporate the modified pigment products of the present invention.

wherein X represents at least an aromatic group or an alkyl group, "polymer" represents repeating monomer or multiple monomer groups or both, optionally having at least one X' group. The total monomer repeating units is from about 1 to about 500. R represents hydrogen, a bond, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aromatic group. When X represents an alkyl group, the "polymer" preferably has no ionic or ionizable group. X' represents an aromatic group or alkyl group and each X' and X can be the same or different. X and/or X' can be substituted or unsubstituted and can include substituted groups such as an ester group, an amide group, an ether group, and the like. The substituted groups can be linked to "polymer". Also, when R represents a bond, the available bond can be attached to the pigment.

The present invention also relates to ink compositions containing at least one modified pigment product of the present invention and at least one ink vehicle.

The present invention also relates to coating compositions comprising at least one modified pigment product of the present invention and at least one coating vehicle.

The present invention also relates to toner compositions containing at least one modified pigment product of the present invention and resin particles.

Also, the present invention relates to a rubber products, polymer (e.g., plastics) products, and films containing conventional ingredients in combination with at least one modified pigment product of the present invention.

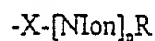
It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide further explanation of the present invention, as claimed.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

The present invention in general relates to various types of modified pigment products which are preferably capable of dispersing in a variety of materials including, but not limited to, liquids (aqueous and non-aqueous), polymers (e.g., thermoplastics and thermosets), elastomers (e.g., synthetic and/or natural rubbers), coatings (e.g., paints), inks (e.g., printing inks and inkjet inks), liquid and solid toners, films, and the like. The pigments are modified such that chemical groups (e.g., polymeric and organic) are attached onto the pigment which provides a more stable attachment of the groups onto the pigment compared to adsorbed groups, e.g., polymers, surfactants and the like.

In each of the following formulas, -X is attached directly to the pigment and -X' can be directly attached to the pigment.

One preferred modified pigment product is a pigment having attached at least one group comprising the formula:



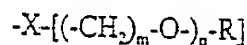
In an additional embodiment of the present invention, the modified pigment product can be a pigment having attached at least group comprising the formula:



wherein X represents an aromatic group or an alkyl group; A represents an alkylene oxide group of from about 1 to about 12 carbons; p represents an integer of from 1 to 500, and R represents hydrogen, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aromatic group. A can be the same or different when p is greater than 1. X can be substituted or unsubstituted and can include substituted groups such as an ester group, an amide group, an ether group, a carbonyl group, an aryl group, an alkyl group and the like. The substituted groups can be attached or linked to A.

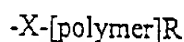
Examples of preferred alkylene groups include, but are not limited to, $-CH_2-CH_2-O-$; $-CH(CH_3)-CH_2-O-$; $-CH_2CH_2CH_2-O-$; or combinations thereof.

In another embodiment of the present invention, the modified pigment product can be a pigment having attached at least one group comprising the formula:



wherein X is described above, and for instance can represent an aromatic group or an alkyl group as described earlier, m is an integer of from 1 to 12, preferably 2 or 3, p is an integer of from 1 to 500, and R is described above, and for instance can be hydrogen, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aromatic group. Examples of R substituents include, but are not limited to, hydrogen, methyl, ethyl, butyl, or propyl groups. p can be 1-25, 26-50, 51-75, 76-100, and 101-500, and is preferably 5 to 50. Particularly preferred groups of this formula are where X is a benzene group, m is 1 to 5, and more preferably 2 or 3, p is 5 to 50, more preferably 44-45, and R is hydrogen or a methyl group. Another preferred group is where m is 2, p is 7, R is a methyl group, and X is a benzene group.

In yet another embodiment of the present invention, the modified pigment product can be a pigment having attached at least one polymeric group, wherein the polymeric group comprises the formula:



wherein X is described above, and for instance can represent at least an aromatic group or at least an alkyl group as described earlier, "polymer" comprises repeating monomer groups or multiple monomer groups or both, optionally having at least one -X' group. The 'polymer' can be substituted or unsubstituted with additional groups, and R is described above, and for instance can represent hydrogen, a bond, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aromatic group. When X represents an alkyl group, the "polymer" preferably has no ionic or

The polymeric groups of the present invention can be prepared in a number of ways and such ways are known to those skilled in the art. The above referenced KIRK-OTHMER section, Modern Plastics Encyclopedia, and C.A. Daniels' reference provide methods in which these polymeric groups can be prepared.

5 The polymeric group is preferably a polyolefin group, a polyurethane group, a polystyrenic group, a polyacrylate group, a polyamide group, a polyester group, or mixtures thereof. Examples of R groups can be the same as previously described above. p can be 1-25, 26-50, 51-75, 76-100, 101-500, and is preferably 1 to 100, and more preferably 5 to 50.

10 The pigment to be modified can be, but is not limited to, pigments traditionally used in ink compositions (including inkjet ink compositions), coating compositions (including paint formulations), liquid and solid toners, films, plastics, rubbers, and the like.

Examples include, but are not limited to, black pigments (e.g., carbon products like carbon black) and other colored pigments (e.g., polymeric and organic pigments).

15 The desired colored pigment may be chosen from a wide range of conventional colored pigments. The colored pigment can be blue, black, white, brown, cyan, green, violet, magenta, red, yellow, as well as mixtures thereof. Suitable classes of colored pigments include, for example, anthraquinones, phthalocyanine blues, phthalocyanine greens, diazos, monoazos, pyranthrones, perylenes, heterocyclic yellows, quinacridones, and (thio)indigoids. Representative examples of phthalocyanine blues include copper phthalocyanine blue and derivatives thereof (Pigment Blue 15).
20 Representative examples of quinacridones include Pigment Orange 48, Pigment Orange 49, Pigment Red 122, Pigment Red 192, Pigment Red 202, Pigment Red 206, Pigment Red 207, Pigment Red 209, Pigment Violet 19 and Pigment Violet 42. Representative examples of anthraquinones include Pigment Red 43, Pigment Red 194 (Perinone Red), Pigment Red 216 (Brominated Pyanthrone Red) and Pigment Red 226 (Pyranthrone Red). Representative examples of perylenes include Pigment Red
25 123 (Vermillion), Pigment Red 149 (Scarlet), Pigment Red 179 (Maroon), Pigment Red 190 (Red), Pigment Violet, Pigment Red 189 (Yellow Shade Red) and Pigment Red 224. Representative examples of thioindigoids include Pigment Red 86, Pigment Red 87, Pigment Red 88, Pigment Red 181, Pigment Red 198, Pigment Violet 36, and Pigment Violet 38. Representative examples of heterocyclic yellows include Pigment Yellow 1, Pigment Yellow 3, Pigment Yellow 12, Pigment
30 Yellow 13, Pigment Yellow 14, Pigment Yellow 17, Pigment Yellow 65, Pigment Yellow 73, Pigment Yellow 74, Pigment Yellow, Pigment Yellow 117, Pigment Yellow 128 and Pigment Yellow 138. Such pigments are commercially available in either powder or press cake form from a number of sources including, BASF Corporation, Engelhard Corporation and Sun Chemical Corporation. Examples of other suitable colored pigments are described in the *Colour Index*, 3rd
35 edition (The Society of Dyers and Colourists, 1982). Representative examples of black pigments

pigment. Preferred reaction media include water, any medium containing water, and any medium containing alcohol. Water is the most preferred medium.

To prepare the above modified pigment products, the diazonium salt need only be sufficiently stable to allow reaction with the pigment. Thus, that reaction can be carried out with some diazonium salts otherwise considered to be unstable and subject to decomposition. Some decomposition processes may compete with the reaction between the pigment and the diazonium salt and may reduce the total number of groups attached to the pigment. Further, the reaction may be carried out at elevated temperatures where many diazonium salts may be susceptible to decomposition. Elevated temperatures may also advantageously increase the solubility of the diazonium salt in the reaction medium and improve its handling during the process. The pigment can be reacted with a diazonium salt when present as a dilute, easily stirred, aqueous slurry, or as a more concentrated highly mixed slurry in water.

A preferred method of preparing the modified pigment products involves reducing the pigments to be modified to a size desirable for the particular end use application. If, of course, the pigment is already of an appropriate size, then no reduction in size is necessary. Generally, the size of the pigment can be the same size as the pigment sizes used conventionally for the particular end use applications. For instance, the average particle size of the pigment can be about 10 microns or less, and preferably about 5 microns or less. Preferably, for instance, in inkjet ink applications, the average pigment particle size is preferably less than about 1 micron and more preferably less than about 0.5 micron (e.g., a preferred range is about 0.01 micron to less than about 1 micron), and is preferably less than about 10 microns for coatings, toner, polymer, and rubber applications. If size reduction of the pigment to be modified is preferred, any method of reducing size can be used such as those described in T.C. Patton, "Paint Flow and Pigment Dispersion," 2nd ed., Wiley, NY (1979), incorporated herein by reference.

To attach a group having one or more of the formulas described above, a surfactant or polymer may be introduced to or contacted with the pigments. The surfactant or polymer comprises an organic group or polymeric group having at least one primary amine. A sufficient amount of time is provided to preferably adsorb the surfactant or polymer onto the pigment. Preferably, after adsorption occurs, a diazonium reaction can be conducted as described in U.S. Patent Nos. 5,571,311 and 5,630,868, as well as 5,554,739 and PCT Publication WO-96/18688, all incorporated herein in their entirety by reference. In more detail, the preferred means of attaching the surfactant or polymer onto the pigments is by grinding, or reducing in size by other suitable mechanical or chemical means, the pigment in the presence of a solvent (e.g., aqueous or non-aqueous), preferably water. The surfactant or polymer can also be present during this size reduction step. Alternatively, the surfactant or polymer may be added after the size reduction step. An aqueous solution of a nitrite and an acid

5 The modified pigment particles can then be subsequently subjected to cleaning procedures (e.g., washing or precipitation) which will remove substantially any excess reactants and unattached dispersants. The remaining slurry containing the modified pigment products can then be added to either aqueous or non-aqueous media and preferably with little or mild agitation to form stable (electrostatic, steric, and/or electrosteric) dispersions for a variety of end uses as described above.

10 The pigment products may be purified by washing, such as by filtration, centrifugation, or a combination of the two methods, to remove unreacted raw materials, byproduct salts and other reaction impurities. The products may also be isolated, for example, by evaporation or it may be recovered by filtration and drying using known techniques to those skilled in the art. Dispersions of the pigments of the present invention may be further purified or classified to remove impurities and other undesirable free species which can co-exist in the dispersion as a result of the manufacturing process. In a preferred embodiment, the cationic pigment dispersions are subject to a classification step, such as centrifugation, to substantially remove particles having a size above about 1.0 micron, preferably above about 0.5 micron. In addition, the dispersion is preferably purified to remove any
15 undesired free species, such as unreacted treating agent. Known techniques of ultrafiltration/diafiltration using a membrane or ion exchange may be used to purify the dispersion and remove a substantial amount of free ionic and unwanted species. Also preferred is an optional exchange of counterions whereby the counterions that form a part of the surface-modified pigment are exchanged or substituted with alternative counterions utilizing known ion exchange techniques
20 such as ultrafiltration, reverse osmosis, ion exchange columns and the like. Particular examples of counterions that can be exchanged include, but are not limited to, Na^+ , K^+ , Li^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , NO_2^- , acetate, carboxylate, and Br^- . Such additional classification and purification methods are more fully described in U. S. Patent Application No. 09/240,291, filed January 29, 1999, the disclosure of which is fully incorporated herein by reference.

25 Uses of the Modified Pigment Products

The modified pigment products of this invention may be used in the same applications as conventional pigments, like carbon blacks. The groups attached to the pigment, however, can be used to modify and improve the properties of a given pigment for a particular use.

30 Modified pigment products according to the invention can be used in a number of end use applications. These uses include, for example, plastic compositions, aqueous and non-aqueous inks, aqueous and non-aqueous coatings, rubber compositions, toner compositions, paper products, and textile and fiber compositions. The following paragraphs describe these uses generally and examples of each are shown below.

In general, an ink consists of four basic components: (1) a colorant, (2) a vehicle or varnish which functions as a carrier during printing, (3) additives to improve printability, drying, and the like, and (4) solvents to adjust viscosity, drying and the compatibility of the other ink components. For a general discussion of the properties, preparation and uses of inks, see *The Printing Manual*, 5th Ed., Leach et al, Eds. (Chapman and Hall, 1993) incorporated herein by reference. Various ink compositions are also disclosed, for example, in United States Patents Nos. 2,833,736; 3,607,813; 4,104,833; 4,770,706; and 5,026,755, incorporated in their entirety herein by reference.

The modified pigment products of the invention, either as predispersion or as a solid, can be incorporated into an ink formulation using standard techniques. Use of a water dispersible or solvent-dispersible modified pigment product of the invention can provide a significant advantage and cost savings by reducing or eliminating the milling steps generally used with other conventional pigments.

Flexographic inks represent a group of ink compositions. Flexographic inks generally include a colorant, a binder, and a solvent. The modified pigment products of the invention are useful as flexographic ink colorants.

The modified pigment products of the invention can be used in news inks. For example, a news ink composition may comprise an ink vehicle (e.g., water), the modified pigment products of the invention, a resin, and optional conventional additives such as antifoam additives or a surfactant.

The modified pigment products of the invention may also be used in phase change (hot melt) inks. Phase change inks generally include at least one colorant and at least one phase change or wax carrier (e.g., a fatty amide-containing material like a mixture of a tetra amide compound and a mono-amide compound, or an alkanolamides and polyethylene glycol mixture). The phase change ink is in a solid phase at ambient temperature and in a liquid phase at an elevated operating temperature of the printer. When the ink is heated it melts to form a low viscosity fluid that can be ejected as droplets. Upon jetting, heated droplets impact on a substrate, and cool to ambient temperature forming films of uniform thickness. Subsequent impaction of the droplets on the substrate may also occur, depending upon the type of printer used. Use of a modified pigment product can provide a significant advantage in dispersion stability and carrier compatibility over conventional pigments and in light-fastness over dyes.

The modified pigments of the present invention can also be used in lithographic or flexographic printing. For example, the ink or fountain solution used in the printing process can contain the modified pigments of the present invention.

The modified pigments of the present invention can also be used in the manufacture of lithographic printing plates, such as infrared or near-infrared laser-imageable printing plates. Typically, imaging occurs when the plate is exposed to radiation having wavelengths of between 800 and 1100 nm. Generally, an infrared or near-infrared laser-imageable lithographic printing plate

significant advantage and cost savings by reducing or eliminating the steps generally used to disperse other conventional pigments.

5 The paper products of the invention may incorporate other known paper additives such as sizing agents, retention aids, fixatives, fillers, defoamers, deflocculating agents, and the like. Advantageously, the water or solvent dispersible modified pigment products discussed above are retained more efficiently at low loading levels when compared to the untreated pigments when retention aids and acidic or alkaline sizing agents are used.

10 The modified pigment products of the invention may also be used, as with conventional pigments, as pigments, fillers, and reinforcing agents in the compounding and preparation of rubber compositions. Accordingly, the invention relates to a rubber or elastomeric composition containing at least one rubber or elastomer and at least one modified pigment.

15 Carbon blacks, for example, are useful in the preparation of rubber vulcanizates such as those in tires. It is generally desirable in the production of tires to utilize carbon blacks which produce tires with satisfactory abrasion resistance and hysteresis performance. The treadwear properties of a tire are related to abrasion resistance. The greater the abrasion resistance, the greater the number of miles the tire will last without wearing out. The hysteresis of a rubber compound means the difference between the energy applied to deform a rubber compound, and the energy released as the rubber compound recovers to its initial undeformed states. Tires with lower hysteresis values reduce rolling resistance and therefore are able to reduce the fuel consumption of the vehicle utilizing the tire. Thus, it is particularly desirable to have carbon black products capable of imparting greater abrasion resistance and lower hysteresis in tires.

20 The modified pigment products, and preferably the modified carbon black products of this invention are useful in both natural and synthetic rubber compositions or mixtures of natural and synthetic rubbers. Carbon black products comprising an aromatic sulfides group are preferred for this use. The carbon black products of the invention can be used in rubber compositions which are sulfur-cured or peroxide-cured.

25 The modified pigment products may be mixed with natural or synthetic rubbers by normal means, for examples by milling. Generally, amounts of the modified pigment product ranging from about 10 to about 250 parts by weight can be used for each 100 parts by weight of rubber in order to impart a significant degree of reinforcement. It is, however, preferred to use amounts varying from about 20 to about 100 parts by weight of carbon black per 100 parts by weight of rubber and especially preferred is the utilization of from about 40 to about 80 parts of carbon black per 100 parts of rubber.

30 Rubbers suitable for use with the present invention are natural rubber and its derivatives such as chlorinated rubber. The modified pigment products of the invention may also be used with

Wiles and Sons, 1979), incorporated herein by reference. Use of a water or solvent dispersible modified pigment product discussed above provides a method for coloring these materials with a lightfast colorant.

5 The present invention also relates to toner compositions comprising toner resin particles and the modified pigment particles of the present invention. Conventional additives as described in U.S. Patent Nos. 5,278,018; 5,510,221; 5,275,900; 5,571,654; and 5,484,575; and EP O 270-066A1 can be used and these patents are incorporated herein by reference.

10 The present invention also relates to an inkjet ink composition comprising an aqueous or non-aqueous vehicle and a modified pigment product. In contrast to conventional pigments, the modified pigment products for use in the inkjet ink of the present invention are not difficult to disperse in an aqueous or non-aqueous vehicle. The modified pigment products do not necessarily require a conventional milling process, nor are additional dispersants necessarily needed to attain a usable ink. Preferably, the modified pigment products only require low shear stirring or mixing to readily disperse the pigment in water or other solvent.

15 Formation of an inkjet ink containing a vehicle and stably dispersed modified pigment product as pigment can be preformed with a minimum of components and processing steps when the above modified pigment products are utilized. Such an ink may be used in any inkjet printer known in the art. Preferably, in inkjet inks of the present invention, the modified pigment products are present in an amount of less than or equal to 20% - 25% by weight of the inkjet ink. It is also within
20 the bounds of the present invention to use an inkjet ink formulation containing a mixture of unmodified pigment with the modified pigment products of the present invention. Common additives such as those discussed below may be added to the dispersion to further improve the properties of the inkjet ink.

25 In particular, a humectant may be added to reduce the rate of evaporation of water in the ink to minimize clogging. If the ink begins to dry out, the humectant concentration increases and evaporation decreases further. Humectants may also affect other properties of the ink and prints made therefrom, such as viscosity, pH, surface tension, optical density, and print quality. Preferred humectants include ethylene glycol, propylene glycol, diethylene glycols, glycerine, dipropylene glycols, polyethylene glycols, polypropylene glycols, amides, ethers, carboxylic acids, esters,
30 alcohols, organosulfides, organosulfoxides, sulfones, alcohol derivatives, carbitol, butyl carbitol, cellosolve, ether derivatives, amino alcohols, and ketones.

35 Biocides such as benzoate or sorbate salts are important in preventing bacterial growth. Bacteria are often larger than ink nozzles and can cause clogging and other problems. Binders attach to the substrate to hold the colorant on the paper. Examples include polyester, polyester-melanine, styrene-acrylic acid copolymers, styrene-acrylic acid-alkyl acrylate copolymers, styrene-maleic acid

Example 1: Preparation of Surfactant-Adsorbed Carbon Black Dispersions

Various amounts (Table 1) of carbon black, having a nitrogen surface area of 200 and a DBPA of 122 g/100 ml, a nonionic surfactant (IL-2798 from ICI Surfactants) described as an ester product of an amino benzoic acid and a polyethylene glycol methyl ether; MW of ~1,000 g/mole, and distilled water were mixed together and placed in stainless steel midget mills (2 1/16" height by 2 3/32" internal diameter). Two hundred grams of 3/16" stainless steel shot were added and the mill was capped and put in a Red Devil #30-5100 paint shaker. The samples were shaken for 1 h. before being removed and filtered through a paint filter to separate the slurries from the steel shot. An aliquot of the dispersions was analyzed for the amount of particles below 1 μ m, after the initial dispersion and 24 h. later, using a Zeiss light microscope containing a calibrated ocular lens. It was found that the amount of particles below 1 μ m was constant, regardless of the time period after dispersing. Results are set forth in Table 1.

Table 1

Sample #	Carbon Black (g)	Surfactant (g)	Water (g)	Amount of Particles Below 1 μ m (%)
1A	6	0	34	<5
1B	2	4	34	80
1C	4	8	28	90
1D	6	12	22	90
1E	8	16	16	98

This example shows that stable, conventional dispersions can be prepared with carbon black, surfactant, and water using mechanical energy, and that without a surfactant the carbon black does not disperse or form a stable dispersion.

Example 2: Preparation of Chemically-bonded Surfactants to Carbon Black and Resulting Dispersions

Samples 1B-E were added to distilled water in a Pyrex beaker and heated to 70°C. Various amounts of sodium nitrite (Table 2) were added to the hot slurry with rapid mixing using a magnetic stir bar. Within one minute the slurries began to froth generating nitrogen gas. The reaction was

Table 3

Sample #	Stability* as a function of Sodium Chloride Concentration (below)					
	0	0.001 M	0.01 M	0.1 M	1 M	2 M
1A	Y	Y	Y	N	N	N
1B	Y	Y	Y	N	N	N
1C	Y	Y	Y	N	N	N
1D	Y	Y	Y	N	N	N
1E	Y	Y	Y	N	N	N
2B	N	N	N	N	N	N
2C	Y	Y	Y	Y	Y	Y
2D	Y	Y	Y	Y	Y	Y
2E	Y	Y	Y	Y	Y	Y

* Stability is being reported as Y = Yes, stable or N = Not stable

This example shows that carbon black lacking surfactant and with adsorbed surfactants are dependent on the media, and that above 0.01M concentration of sodium chloride, the dispersions become unstable. Last, the example demonstrates that when the surfactant is covalently attached (chemically bonded) to the surface of carbon black, the resulting dispersion is stable at all salt concentrations and that the surfactant is not in an equilibrium between the media and the carbon surface, as is the case with adsorbed surfactants. Also, a sufficient amount of surfactant, conditions to obtain samples 2C-2E, is needed to provide dispersion stability. The mechanism for stabilization with the nonionic surfactants, adsorbed or bonded, is steric and not ionic.

Example 4: Stability of Dispersions of Carbon Black with Chemically-bonded and Adsorbed Surfactants in Non-Aqueous Media

Samples 1A, 1E and 2E were dried and dispersed in different nonaqueous solvents to determine the effect of the surfactant on the resulting dispersion stabilities. The solids were added to the liquid media in a test tube stoppered and thoroughly shaken by hand. The concentrations and procedures were similar to those of Example 3. Results are reported in Table 4.

Table 5

Sample	Mean Particle Size (μm)	Largest Particle Size* (μm)	<u>Xerox Paper</u>		<u>Plover Paper</u>	
			Dry Time		Dry Time	
			O.D.	(H)	O.D.	(H)
1E	0.17	0.69	1.03	3	1.14	3
2E	0.16	0.58	1.07	3	1.14	3

* largest particles as detected by Microtrac UPA instrument

This example shows that inkjet inks can be made with the dispersions of carbon black with adsorbed and bonded surfactants. The resulting print can achieve a good optical density and print waterfastness properties.

Example 6: Inkjet Inks Containing Dispersions of Carbon Black with Chemically-bonded and Adsorbed Surfactants

Inkjet inks were made and tested in a similar manner as Example 5, except that 10% (final (w/w ink) diethylene glycol was used in place of 2-pyrrolidone. Also, a highlighter (Avery HILITER®, series #24-0XX) was rubbed over the resulting print to determine highlighter smear. The highlighter was rubbed over the print two times and the amount of black runoff was noted. Dry time was determined as a function of time. One ml of distilled water was applied to a 1/4" line of print, and the time noted when no visible black runoff occurred. Results are reported in Table 6.

Table 6

Sample	<u>Xerox Paper</u>		<u>Plover Paper</u>	
	O.D.	Dry Time	O.D.	Dry Time
1E	1.08	24 h	1.11	24 h
2E	0.97	5 min	1.03	5 min

This example shows that inkjet inks, besides those of Example 5, can be made with the dispersions of carbon black with adsorbed and bonded surfactants. The resulting print can achieve a fair optical density and print waterfastness, and excellent highlighter smear resistance. The dry time was significantly faster for the prints made with the dispersion of carbon black with the bonded surfactant compared to those for the equivalent having only the adsorbed surfactant.

Example 9: Preparation of Carbon Black Dispersions

The purpose of this example was to prepare dispersions of carbon black and of carbon black with non-chemically bonded ABT ester. Six grams of a carbon black described in Example 1 was added to TPM (34 g) and milled using a Midget mill, the procedure was described in Example 1. The product is designated Example 9A. In addition, the same carbon black (5.2 g) and ABT (0.8 g) and TPM (34 g) were also similarly milled. The product is designated Example 9B.

Example 10: Properties of Inks Containing Chemically-Bonded Polymer to Carbon Black Pigments

The purpose of this example was to contrast properties of inks containing different carbon black products. One ink contains a carbon product having a chemically-bonded polymer (Example 8), another has carbon black (Example 9A), and the last ink contains a carbon black and polymer mixture (Example 9B). The inks were made by mixing the solids (w/w) with TPM. A drop of the resulting inks were put between two glass slides and observed using a light microscope, with a calibrated ocular lens, at a magnification of 40x power. The ink with Example 8 was dispersed (Brownian movement with particles less than 1 μ m in diameter), while the other inks flocculated (the carbon blacks networked together to form a structure with a size above five μ m). Results are shown in Table 7.

Table 7: Observations

Sample No.	8	9A	9B
Observation	Dispersed	Flocculated and Settled	Flocculated

After storing at 70°C for a week, Example 8 was still well dispersed upon observation under the microscope while 9A and 9B settled.

The 7% products in TPM were drawn down on white paper (form 3NT-4 Ink Test Regular Bond paper) and brown paper (form 3NT-5 Ink Test Kraft paper), both from Leneta Co., using a 3 mil Bird applicator with a Byk-Gardner automatic draw down device. The resulting ink films were measured for optical density using the optical densiometer described in Example 5. The results are reported in Table 8.

Example 14: Properties of Inks Containing Chemically-Bonded Polymer and Ionic Groups, and Chemically-Bonded Ionic Groups to Carbon Black Pigments

The purpose of this example was to contrast properties of an ink with a carbon product having a chemically-bonded polymer and ionic groups against one with just ionic groups. Examples 12 and 13 were mixed into distilled water resulting in dispersions having 5% solids (w/w). The resulting inks were drawn down on Xerox 4024 paper and the dry time (waterfastness) and optical densities of the films were measured, all methods and instruments were previously described in Example 5. The results are shown in Table 8.

Ink with Example	Optical Density	Dry Time (min)
12	1.65	5
13	1.54	>5

The results show that the film formed from ink containing carbon black with chemically-bonded polymer and ionic groups dried faster, possibly due to its penetration into the paper compared to that formed from dispersions having just an ionic group. This example also shows that polymer and ionic groups can both be present on a pigment.

Example 15: Infrared Absorptive Coating Composition

This example demonstrates that a modified carbon black prepared via the method of Example 2 can be used in the formulation of an infrared absorptive coating. The modified carbon black dispersion 2E should be dried prior to preparation of the coating. A useful infrared sensitive coating can be prepared by mixing together, with minor expenditure of energy, the ingredients shown below in parts by weight. Nitrocellulose E950 is available from Wolff Walsrode and Cymel 301 is available from Dyno Cyanamide.

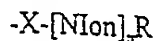
2-butanone	289.9
Dry carbon black 2E	5-10
Nitrocellulose E950	3.68
Cymel 301	0.69
p-toluene sulfonic acid	0.15

The coating composition can be applied to a substrate via a knife coater or wire wound rod to give a wet coating thickness of 20 microns. Examples of substrates that can be used are polyester or grained anodized aluminum.

To improve adhesion of the infrared adsorptive layer to the substrate, it may be advantageous to apply an additional layer to the substrate prior to applying the infrared adsorptive layer. This

WHAT IS CLAIMED IS:

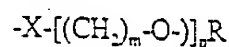
1. A modified pigment product comprising a pigment having attached at least one group comprising the formula:



wherein X is attached to the pigment and comprises at least an aromatic group or at least an alkyl group, Nlon comprises at least one type of non-ionic group, R is hydrogen or comprises an aromatic group or an alkyl group, and p represents an integer of from 1 to 500.

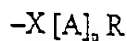
2. The modified pigment of claim 1, wherein Nlon is a C₁-C₁₂ alkyl group or a C₁-C₁₂ alkylene oxide group.
3. The modified pigment product of claim 1, wherein said non-ionic group further comprises a functional group.
4. The modified pigment product of claim 1, wherein said non-ionic group is a glycol group.
5. The modified pigment product of claim 1, wherein X is an aromatic group.
6. The modified pigment product of claim 1, wherein p is 1 to 50.

7. A modified pigment product comprising a pigment having attached at least one group comprising the formula:



wherein X comprises an aromatic group or an alkyl group, m is an integer of from 1 to 12, p is an integer from 1 to 500, and R is hydrogen or comprises an alkyl group or an aromatic group.

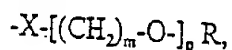
8. The modified pigment product containing a pigment having attached at least one group comprising the formula:



wherein X is attached to the pigment and comprises at least an aromatic group or at least an alkyl group; A represents an alkylene oxide group of from about 1 to about 12 carbons; p represents an integer of from 1 to 500; and R represents hydrogen, a substituted or unsubstituted alkyl group or

alkyl group or at least an aromatic group; wherein X' comprises at least an aromatic group or at least an alkyl group, and each X' and X can be the same or different; and the total amount of monomer groups that comprise "polymer" is not greater than about 500 monomer repeating units, and when R represents a bond, R optionally bonds to said pigment.

20. An ink composition comprising a) at least one liquid vehicle; b) at least one modified pigment product comprising a pigment having attached at least one group comprising the formula:



wherein X is attached to the pigment and comprises at least an aromatic group or at least an alkyl group, m represents an integer of from 1 to 12, p represents an integer of from 1 to 500, and R represents hydrogen, or comprises an alkyl group or an aromatic group.

21. An ink composition comprising a pigment having attached at least one group comprising the formula:



wherein X is attached to the pigment and comprises at least an aromatic group or at least an alkyl group; A represents an alkylene oxide group of from about 1 to about 12 carbons; p represents an integer of from 1 to 500; and R represents hydrogen, a substituted or unsubstituted alkyl group or a substituted or unsubstituted aromatic group wherein A can be the same or different when p is greater than 1.

22. The ink composition of claim 21, wherein said liquid vehicle is aqueous.

23. The ink composition of claim 21, wherein said liquid vehicle is non-aqueous.

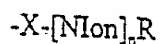
24. The ink composition of claim 21, wherein said ink composition is an inkjet ink composition.

25. The ink composition of claim 21, further comprising at least one humectant, at least one binder, at least one dye, at least one biocide, at least one penetrant, at least one surfactant, or combinations thereof.

26. The ink composition of claim 21, wherein said pigment is carbon black, graphite, vitreous carbon, finely-divided carbon, activated carbon, activated charcoal, or mixtures thereof.

polyurethane group, a polystyrenic group, a polyacrylate group, a polyamide group, a polyester group, polyvinyl (alcohol), or combinations thereof.

37. An ink composition comprising at least one liquid vehicle and a modified pigment product comprising a pigment having attached at least one group comprising the formula:



wherein X is attached to the pigment and comprises at least an aromatic group or at least an alkyl group; Nlon comprises at least one type of non-ionic group; R represents hydrogen or comprises an aromatic group or an alkyl group; and p represents an integer of from 1 to 500.

38. A method to attach at least one group selected from an organic group or polymeric group onto a plurality of pigment comprising reducing the average particle size of said pigment in a solvent and introducing a) at least one surfactant or polymer comprising said group and having at least one primary amine, b) a nitrite, and c) an acid in sufficient amounts together or in any combination to generate a diazonium salt comprising at least said group, and wherein said diazonium salt reacts with said pigment to attach said at least one group onto said pigment.

39. A method of claim 38, wherein at least a portion of said primary amine dispersant adsorbs onto at least a portion of the pigment.

40. The method of claim 38, wherein said primary amine dispersant further contains at least one non-ionic group.

41. The method of claim 38, wherein two or more different primary amine dispersant are introduced.

42. The method of claim 38, further comprising introducing a second diazonium salt comprising a second organic group.

43. The method of claim 38, wherein said primary amine dispersant comprises an aromatic group or an alkyl group.

44. The method of claim 38, wherein said acid is nitric acid or sulfuric acid.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09B C09D G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 18695 A (CABOT CORP) 20 June 1996 (1996-06-20)	1,11, 21-27, 29,38 1-56
Y	the whole document	
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Y	abstract; example 59	1-45
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Y	the whole document	1-44
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

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Authorized officer

Dauksch, H

54. The method of claim 47, further comprising subjecting the plate to a solvent capable of removing portions of the imaged layer(s) defining the pattern.

55. A method of imaging a lithographic printing plate of claim 48, comprising selectively exposing the plate to a laser output in a pattern representing an image to selectively remove or chemically modify at least the radiation-absorptive layer defining the pattern.

56. The method of claim 48, further comprising subjecting the plate to a solvent capable of removing portions of the imaged layer(s) defining the pattern.

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